

Synthesis of Removable and Repositionable Water-Borne Pressure-Sensitive Adhesive Acrylics

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ABSTRACT: This publication shows the synthesis of the water-borne removable pressure-sensitive adhesive (PSA) based on acrylates and the influence of parameters such as internal emulsifiers on peel adhesion on steel and also the influence of *N*-methylol acrylamide and plasticizers on peel adhesion on glass, poly(vinyl chloride), and polypropylene during aging time. Removable and repositionable pressure-sensitive adhesives based on acrylic polymers are used for

the production of removable memo notes, paper and foil labels, double-sided tapes, carrier-free tapes to protective films, and manufacturing aids. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 886–892, 2005

Key words: acrylic; water-borne; pressure-sensitive adhesive; emulsifiers; peel adhesion; removable; monomers; molecular mass; viscosity

INTRODUCTION

The main objective of this work was to develop a water-borne pressure-sensitive adhesive for removable, semi-removable, and repositionable products with peel adhesion on steel and other surfaces such as, for example, glass, poly(vinyl chloride) (PVC), and polypropylene (PP).

Adhesive articles, such as, for example, pressure-sensitive adhesive tapes, are usually firmly bonded to substrates, because subsequent separation of the tapes from the substrates is neither intended nor desired. They are not, in general, removed cleanly from non-paper substrates. Some residue of the adhesive is left on the substrate, thus making its cleaning less effective or more involved. There is a growing need in the market today for environmentally or user-friendly water-borne pressure-sensitive adhesive articles which can be cleanly removed from the substrate during domestic or industrial cleaning processes.¹

Removable water-borne pressure-sensitive adhesives adhered to a backing are those that predictably adhere, yet remain repeatedly peelable, from a variety of substrates over a long period of time without damaging or marring the substrate have many commercial uses. For example, masking tapes, removable labels or office notes, protective foils, and medical tapes all must quickly adhere to metal, paper, plastics, glass, wood, and skin, respectively, but must also peel smoothly away from these varied substrates without

leaving behind any adhesive residue on or damaging the surface of a particular substrate.²

Repositionable water-borne pressure-sensitive adhesives (PSA) are those which allow for placement of an article containing such an adhesive onto a receptor in an exact position, because the article can be adjusted relative to the receptor after initial placement.³ In some instances, the adhesive can be designated repositionable or repeatedly reusable. Such adhesives exhibit aggressive tack but low-peel adhesion properties, thus allowing repeated reusability. Commercial products such as the 3M Post-it™ notes display such adhesive characteristics. Repositionable adhesive systems, however, as used herein, generally display high peel adhesion and elevated shear strength after positioned placement.⁴

The terms removable and repositionable are intended to refer not only to products that can be temporarily adhered to, removed from, and repositioned on diverse substrates sheets but also to products to which substrate sheets can be temporarily adhered, removed, and repositioned.⁵

Classification of pressure-sensitive adhesive according the adhesion properties is shown in Figure 1.

EXPERIMENTAL

The following experiments were conducted for synthesis and modifying of water-borne PSA acrylics: 2-Ethylhexyl acrylate (2-EHA), ethyl acrylate (EA), methyl methacrylate (MMA), vinyl acetate (VA), acrylic acid (AA), and styrene, purchased from Tokyo Chemical Industry Co. During the synthesis of water-borne PSA, unsaturated copolymerizable emulsifier

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monomers synthesized at Chemitec Co. (Germany) were used, as shown in Figure 2.

The initiator Luperox 575 (*tert*-amyl peroxy-2-ethylhexanoate) for synthesis of water-borne acrylics was purchased from Atochem (Germany); the *N*-methylol acrylamide was purchased from American Cyanamid (USA) and the plasticizers, di-*n*-butyl phthalate, diethylhexyl phthalate, and di-*n*-octyl phthalate, were acquired from DSM Coating Resins (Holland).

The dispersion PSA was coated on one polyester foil (36 μm) and dried at 110°C for 10 min. Samples were cut into 1-in. strips and applied to stainless steel or other test substrates. The peel adhesion was measured on a Zwick apparatus after a specified dwell period.

Removability

Pressure-sensitive adhesives were considered removable if they are removed cleanly from a test substrate without causing any damage to the test substrate over a range of peel rates and varied periods of dwell at room temperature.

A strip 2.5 cm in width of the sheet coated with the PSA to be tested was applied to the horizontal surface of a polyester, treated polyester, or other test substrate with at least linear 25 cm in firm contact. Three passes in each direction with a 2-kg hard rubber roller were used to apply the strip. After 1 day or 1 week of dwell, the free end of the coated strip was doubled back nearly touching itself, so the angle of removal is ~ 135 grade. The free end is then pulled by hand at a variety of peel rates. The removability and peel force are judged according to the following ratings and recorded.

180° Peel Adhesion

The sample to be tested consisted of a backing laminated to or coated with a pressure-sensitive adhesive. A stainless steel test panel of at least 5 \times 25 cm was used as the substrate from which the sample was peeled. The last 2.5 cm of the length of the panel was covered with masking tape. Strips of tape samples 2.5 \times 25 cm were adhered by way of the pressure-sensitive adhesive to one major surface of the stainless steel

Kind of PSA	Removability of PSA [N/2.5 cm] (180° peel adhesion)
Excellent permanent	> 14
Permanent	10...14
Semi-removable	6...8
Removable and repositionable	2...4
Excellent removable	<1

Figure 1 Classification of pressure-sensitive adhesive versus peel adhesion.

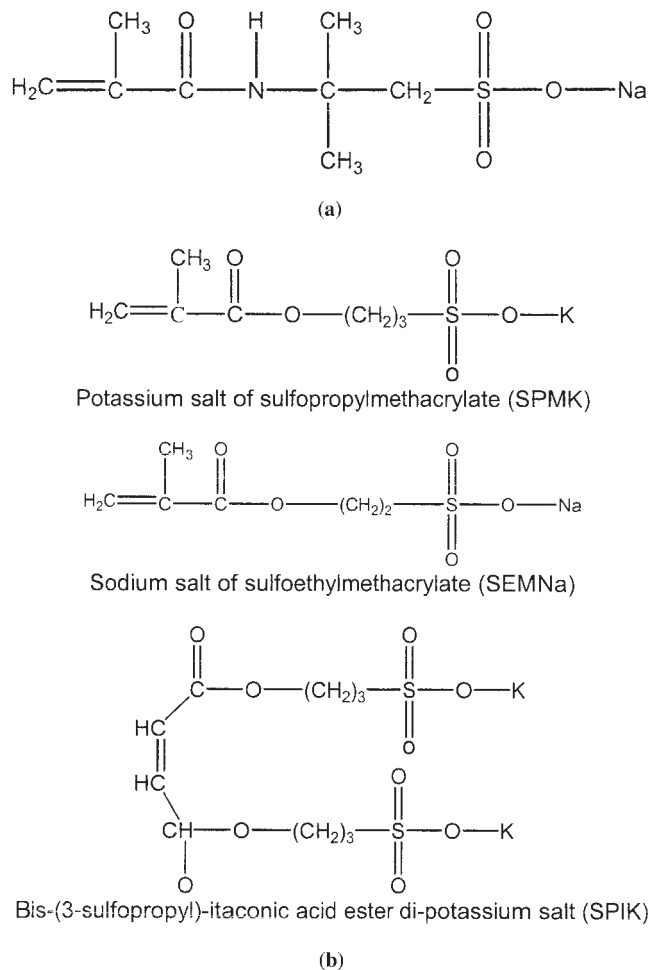


Figure 2 Unsaturated copolymerizable emulsifiers.

test panel such that the end of the sample superimposed the masking tape. The sample of tape was rolled twice with a 4.5-kg roller to firmly bond it to the test panel. The major surface of the test panel not bearing the tape sample was adhered to the surface of peel adhesion tester by means of a double-coated tape. One end of the test sample was separated from the masking tape by hand and peeled at a rate of 305 mm/min through a distance of 25 cm at a peel angle of 180 grade. The initial 2.5 cm of peel data were discarded. The average peel force measured over the remaining peel length was recorded.

RESULTS AND DISCUSSION

The manufacture of removable water-based pressure-sensitive adhesives is being shifted from organic solvent systems to aqueous lattices to reduce air pollution and fire hazard and also to eliminate the rising expense of organic solvents.

TABLE I
Viscosity and Molecular Mass of Synthesized PSA Containing Sodium Salt of 2-Acrylamido-2-methylpropyl Sulfonic Acid (AMPSNa)

PSA No.	Monomers (wt %)							η (mPa s)	M_w (D)
	2-EHA	EA	VA	MMA	Styrene	AA	AMPSNa		
1	47.4	30.0	15.0	5.0	2.0	0.5	0.1	745	512,000
2	47.0	30.0	15.0	5.0	2.0	0.5	0.5	771	533,000
3	46.5	30.0	15.0	5.0	2.0	0.5	1.0	810	602,000
4	46.0	30.0	15.0	5.0	2.0	0.5	1.5	873	659,000
5	45.5	30.0	15.0	5.0	2.0	0.5	2.0	940	712,000
6	45.0	30.0	15.0	5.0	2.0	0.5	2.5	1006	768,000
7	44.5	30.0	15.0	5.0	2.0	0.5	3.0	1055	820,000
8	44.0	30.0	15.0	5.0	2.0	0.5	3.5	1105	885,000
9	43.5	30.0	15.0	5.0	2.0	0.5	4.0	1167	908,000
10	43.0	30.0	15.0	5.0	2.0	0.5	4.5	1180	913,000
11	42.5	30.0	15.0	5.0	2.0	0.5	5.0	1233	941,000
12	41.5	30.0	15.0	5.0	2.0	0.5	6.0	1280	960,000
13	40.5	30.0	15.0	5.0	2.0	0.5	7.0	1366	995,000

Influence of unsaturated copolymerizable emulsifier monomer kind and amount of viscosity, molecular mass, and removability of acrylic water-borne pressure-sensitive adhesive

The basic water-borne pressure-sensitive adhesives were synthesized with between 40.5 and 47.4% 2-EHA, 30% EA, 15% vinyl acetate, 5% methyl methacrylate, 2% styrene, 0.5% AA, and between 0.1 and 7.0% unsaturated copolymerizable emulsifiers. The water-borne PSAs were synthesized with solid content on 60 wt % and Luperox 575 amounts of 0.1 wt %. The dosage time was 3 h.

The synthesized water-borne pressure-sensitive adhesives containing unsaturated copolymerizable emulsifiers are shown in Tables I-IV.

Generally, it can be said that the increase of unsaturated emulsifier concentration has a strong impact on viscosity (Fig. 3). The greatest influence on viscosity has a sodium salt of 2-acrylamido-2-methylpropyl sulfonic

acid (AMPSNa) and the lowest influence on Bis-(3-sulfo-propyl)-itaconic acid ester dipotassium salt (SPIK).

The increase in unsaturated emulsifier concentration also had a positive influence on molecular mass of synthesized pressure-sensitive adhesives (Fig. 4). The best unsaturated emulsifier is in this case a sodium salt of AMPSNa.

Figure 5 illustrates how the influence of vinyl-unsaturated emulsifiers on peel adhesion on steel depends on the type of investigated internal emulsifiers and their concentration.

Varying the internal emulsifiers concentration offers an interesting possibility of influencing the peel adhesion. The relatively low peel adhesion is observed for vinyl-unsaturated emulsifier SPMK in amounts between 1.5 and 5% by weight. SPMK was the best internal emulsifier for removable PSA dispersions. The increase of the amount of SPMK above 5 wt % influences very little the removability.

TABLE II
Viscosity and Molecular Mass of Synthesized PSA Containing Potassium Salt of Sulfopropylmethacrylate (SPMK)

PSA No.	Monomers (wt %)							η (mPa s)	M_w (D)
	2-EHA	EA	VA	MMA	Styrene	AA	SPMK		
14	47.4	30.0	15.0	5.0	2.0	0.5	0.1	730	505,000
15	47.0	30.0	15.0	5.0	2.0	0.5	0.5	745	512,000
16	46.5	30.0	15.0	5.0	2.0	0.5	1.0	777	537,000
17	46.0	30.0	15.0	5.0	2.0	0.5	1.5	815	610,000
18	45.5	30.0	15.0	5.0	2.0	0.5	2.0	860	659,000
19	45.0	30.0	15.0	5.0	2.0	0.5	2.5	905	703,000
20	44.5	30.0	15.0	5.0	2.0	0.5	3.0	947	746,000
21	44.0	30.0	15.0	5.0	2.0	0.5	3.5	985	806,000
22	43.5	30.0	15.0	5.0	2.0	0.5	4.0	1020	822,000
23	43.0	30.0	15.0	5.0	2.0	0.5	4.5	1056	843,000
24	42.5	30.0	15.0	5.0	2.0	0.5	5.0	1097	867,000
25	41.5	30.0	15.0	5.0	2.0	0.5	6.0	1110	880,000
26	40.5	30.0	15.0	5.0	2.0	0.5	7.0	1180	901,000

TABLE III
Viscosity and Molecular Mass of Synthesized PSA Containing Sodium Salt of Sulfoethylmethacrylate (SEMNa)

PSA No.	Monomers (wt %)							η [mPa s]	M_w (D)
	2-EHA	EA	VA	MMA	Styrene	AA	SEMNa		
27	47.4	30.0	15.0	5.0	2.0	0.5	0.1	740	510,000
28	47.0	30.0	15.0	5.0	2.0	0.5	0.5	765	521,000
29	46.5	30.0	15.0	5.0	2.0	0.5	1.0	788	548,000
30	46.0	30.0	15.0	5.0	2.0	0.5	1.5	836	622,000
31	45.5	30.0	15.0	5.0	2.0	0.5	2.0	877	680,000
32	45.0	30.0	15.0	5.0	2.0	0.5	2.5	903	715,000
33	44.5	30.0	15.0	5.0	2.0	0.5	3.0	967	763,000
34	44.0	30.0	15.0	5.0	2.0	0.5	3.5	1005	803,000
35	43.5	30.0	15.0	5.0	2.0	0.5	4.0	1035	847,000
36	43.0	30.0	15.0	5.0	2.0	0.5	4.5	1067	869,000
37	42.5	30.0	15.0	5.0	2.0	0.5	5.0	1082	901,000
38	41.5	30.0	15.0	5.0	2.0	0.5	6.0	1100	930,000
39	40.5	30.0	15.0	5.0	2.0	0.5	7.0	1136	952,000

Influence of *N*-methylol acrylamide monomer and diverse plasticizers of viscosity, molecular mass, and removability of acrylic water-borne pressure-sensitive adhesive

One of the possibilities of reducing the water-based PSA peel adhesion lies in the variation of the used of *N*-methylol acrylamide⁶ and plasticizer. The *N*-methylol acrylamide was used in amounts between 0.5 and 5 wt % and the plasticizer in amounts between 10 and 30 wt %. A new removable dispersion is developed by using the best removability emulsifier SPMK and known plasticizers such as di-*n*-butyl phthalate, diethylhexyl phthalate, and di-*n*-octyl phthalate.

The basic water-borne pressure-sensitive adhesives were synthesized with between 39.5 and 44.0% 2-EHA, 30% EA, 15% vinyl acetate, 3.0% emulsifier monomer SPMK, 5% methyl methacrylate, 2% styrene, 0.5% AA, and between 0.5 and 5.0% *N*-methylol acryl-

amide (*N*-MA). The water-borne PSAs were synthesized with solid content on 60 wt % and Luperox 575 amount of 0.1 wt %. The dosage time was 3 h.

The synthesized water-borne pressure-sensitive adhesives containing unsaturated copolymerizable emulsifiers are shown in Table V.

As expected, the increase of *N*-methylol acrylamide content positively affects the viscosity of synthesized pressure-sensitive adhesive acrylics.

Figures 6 and 7 illustrate the influence of *N*-methylol acrylamide concentration on molecular mass of investigated water-borne pressure-sensitive adhesive acrylics.

The synthesized water-borne PSA acrylics with high concentration of *N*-methylol acrylamide gives the investigated pressure-sensitive adhesive the higher level of molecular mass.

It was the aim of this work to examine the influence of kind and amount of plasticizers such as di-*n*-butyl

TABLE IV
Viscosity and Molecular Mass of Synthesized PSA Containing Bis-(3-sulfo-propyl)-itaconic Acid Ester Dipotassium Salt (SPIK)

PSA No.	Monomers (wt %)							η (mPa s)	M_w (D)
	2-EHA	EA	VA	MMA	Styrene	AA	SPIK		
40	47.4	30.0	15.0	5.0	2.0	0.5	0.1	728	504,000
41	47.0	30.0	15.0	5.0	2.0	0.5	0.5	739	532,000
42	46.5	30.0	15.0	5.0	2.0	0.5	1.0	760	557,000
43	46.0	30.0	15.0	5.0	2.0	0.5	1.5	795	580,000
44	45.5	30.0	15.0	5.0	2.0	0.5	2.0	823	613,000
45	45.0	30.0	15.0	5.0	2.0	0.5	2.5	859	649,000
46	44.5	30.0	15.0	5.0	2.0	0.5	3.0	875	672,000
47	44.0	30.0	15.0	5.0	2.0	0.5	3.5	891	690,000
48	43.5	30.0	15.0	5.0	2.0	0.5	4.0	923	712,000
49	43.0	30.0	15.0	5.0	2.0	0.5	4.5	944	734,000
50	42.5	30.0	15.0	5.0	2.0	0.5	5.0	960	765,000
51	41.5	30.0	15.0	5.0	2.0	0.5	6.0	987	786,000
52	40.5	30.0	15.0	5.0	2.0	0.5	7.0	999	801,000

The influence of unsaturated copolymerizable emulsifiers on viscosity and molecular mass of synthesized water-borne PSA is shown in Figures 3 and 4.

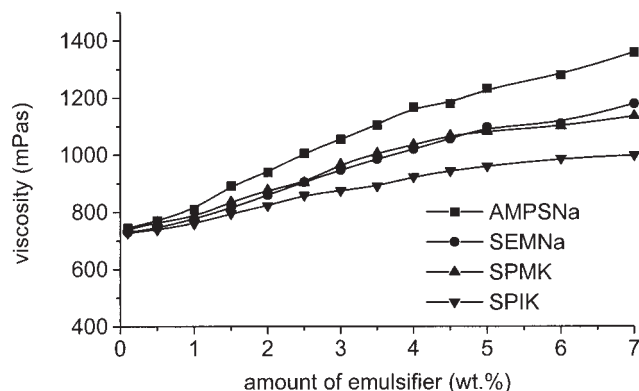


Figure 3 Effect of amount of unsaturated emulsifier on viscosity.

phthalate, diethylhexyl phthalate, and di-*n*-octyl phthalate on peel adhesion of water-borne PSA acrylic formulations. It is known that the use of plasticizers after polymerization improves the removability (reducing of peel adhesion) of pressure-sensitive adhesive. The following trials were conducted with PSA 55 containing 2.0 wt % *N*-methylol acrylamide. The investigated plasticizers were tested in amounts of 10–30 wt % (Fig. 8).

Varying the plasticizer concentration offers an interesting possibility of influencing the peel adhesion. The relatively removable performance was observed for all investigated plasticizers. The best removable properties were given by the trials with di-*n*-octyl phthalate.

Control of the peel adhesion of an emulsion-removable PSA can be achieved by using *N*-methylol acrylamide and plasticizer. The removable water-based PSA was formulated and tested on substrates having different surface energies, for example, PP and PVC. The investigated dispersion contained 2.0 wt % *N*-methylol acrylamide and 20 wt % di-*n*-octyl phthalate (Fig. 9).

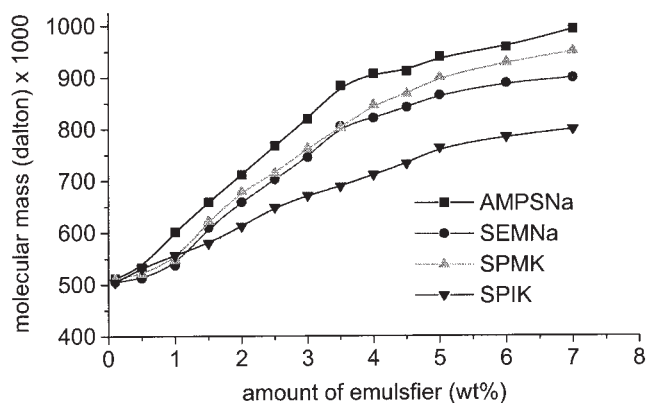


Figure 4 Effect of amount of unsaturated emulsifier on molecular mass.

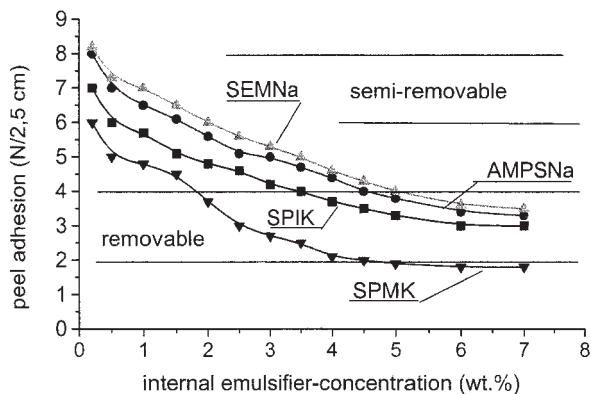


Figure 5 Influence of internal emulsifiers on peel adhesion on steel.

A key property of this type of removable dispersion is that the adhesion peel does not build with time. By using dispersions with *N*-methylol acrylamide and plasticizer di-*n*-butyl phthalate, we have also shown that the peel adhesion of coated samples of PP and PVC does not build significantly during the aging time.

CONCLUSIONS

From the evaluation of the experiments discussed in this publication, the following conclusions can be made:

- An increase of unsaturated emulsifier content increases the viscosity and molecular mass of synthesized water-borne pressure-sensitive adhesives;
- An increase of unsaturated emulsifier content decreases the peel adhesion and improves the removability of acrylics PSA;
- The best results for removability of water-borne PSA were observed with potassium salt of sulfo-propylmethacrylate (SPMK);
- An increase of *N*-methylol acrylamide concentration has a beneficial effect on viscosity and molecular mass of synthesized water-borne PSA acrylics;
- Plasticizer amount positively influences removability of water-borne acrylic pressure-sensitive adhesives. The best removability performance was achieved with di-*n*-octyl phthalate;
- The synthesized water-borne pressure-sensitive adhesives were characterized through a relatively constant level of removability performance on investigated surfaces.

Considering an influence of all the unsaturated emulsifiers, the following conclusions can be drawn:

TABLE V
Viscosity and molecular mass of synthesized PSA containing N-methylol acrylamide

PSA No.	Monomers (wt %)					AA	SPMK	N-MA	η (mPa s)	M_w (D)
	2-EHA	EA	VA	MMA	Styrene					
53	44.0	30.0	15.0	5.0	2.0	0.5	3.0	0.5	870	689,000
54	43.5	30.0	15.0	5.0	2.0	0.5	3.0	1.0	930	765,000
55	42.5	30.0	15.0	5.0	2.0	0.5	3.0	2.0	995	827,000
56	41.5	30.0	15.0	5.0	2.0	0.5	3.0	3.0	1055	881,000
57	40.5	30.0	15.0	5.0	2.0	0.5	3.0	4.0	1122	926,000
58	39.5	30.0	15.0	5.0	2.0	0.5	3.0	5.0	1210	983,000

The influence of *N*-methylol acrylamide concentration on viscosity and molecular mass of synthesized water-borne pressure-sensitive adhesives is shown in Figures 6 and 7.

Undoubtedly, in the case of application of the acrylamide derivative AMPSNa, the hydrogen bonds occurring in a polymer structure have the highest influence on the molecular mass and viscosity increase of water dispersions. In the case of application of SEMNa and SPMK, a very close similarity between them has been noticed. Both emulsifiers have almost the same chemical structure. They differ from each other only in Na or K atoms.

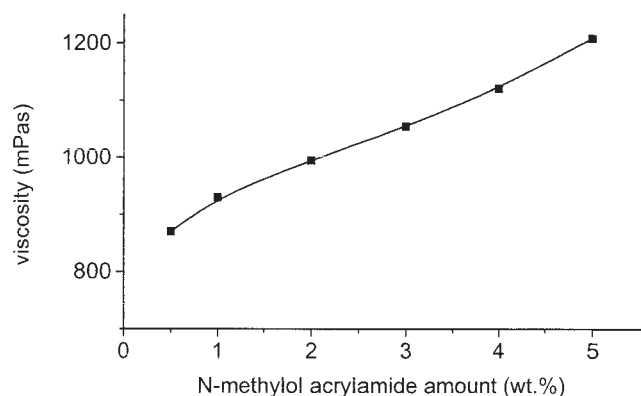


Figure 6 Influence of *N*-methylol acrylamide concentration on viscosity.

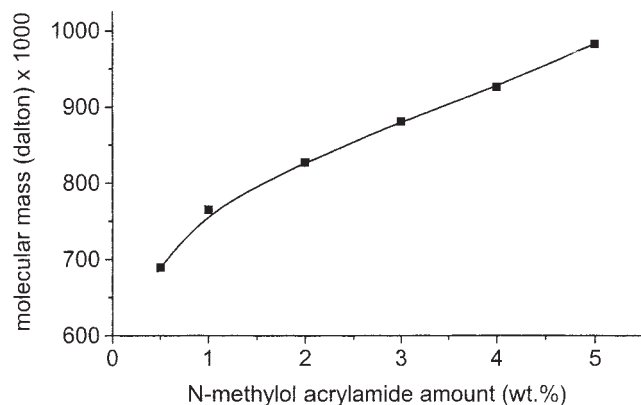


Figure 7 Influence of *N*-methylol acrylamide concentration on molecular mass.

The lowest viscosity and molecular weight (M_w) increase has been observed in the case of SPIK application. It has been caused because of lower reactivity of the alkene double bond, much lower than the typical methacrylic groups occurring in such substances as AMPSNa, SEMNa, and SPMK. Decrease of peel adhesion and increase of removability (Fig. 5) have been undoubtedly connected to the occurrence of Na and K atoms in tested emulsifiers.

On the basis of the previous tests of water-dispersible PSA acrylics, it has been proved conclusively that introduction of organic compounds containing the atom sodium into the system improves adhesion (worsens

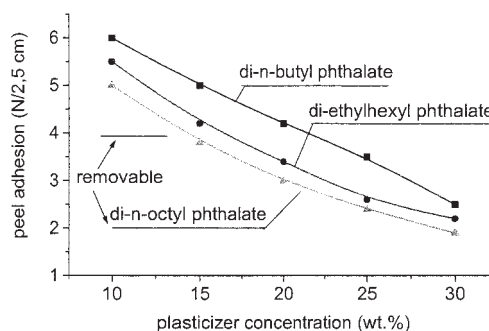


Figure 8 Influence of plasticizer concentration on peel adhesion.

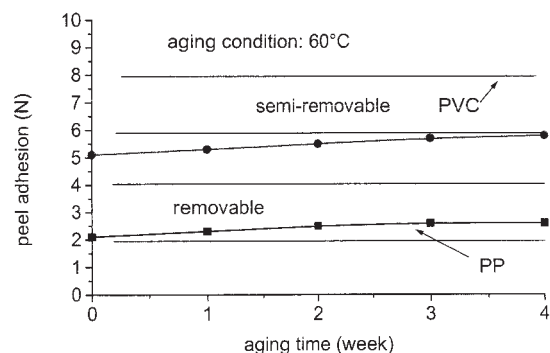


Figure 9 Adhesion performance of a dispersion-removable PSA on PP and PVC substrates.

removability) to various surfaces in comparison with similar compounds containing potassium atoms.

Because of the hydrogen bond's viscosity and M_w , *N*-methylol acrylamide (Figs. 7 and 8) becomes higher. *N*-MAA has also extremely positive influence on pressure-sensitive adhesive cohesion and has often been used as a crosslinking agent.

A wide range of plasticizers have been applied to achieve removability. Better removability in the case of di-*n*-octyl phthalate application than in the case of di-*n*-butyl phthalate application has resulted from the length of polymer carbon chain. Bunching of the carbon chain in diethylhexyl phthalate plasticizer structure raises the peel adhesion much more and decreases removability much more than di-*n*-octyl phthalate.

PROSPECTS FOR REMOVABLE AND REPOSITIONABLE PSA

Removable and repositionable pressure-sensitive adhesives based on polyacrylates will play a major role

in the development and production of a new generation of removable memo notes, paper and foil labels, double-sided tapes, carrier-free tapes, protective foils, and medical tapes.

All the products must quickly adhere to metal, paper, plastics, glass, wood, skin, and other surfaces. The removable acrylic PSAs are characterized by excellent low-tack, high-strength cohesion, low constant level of peel adhesion, and the excellent aging performance at room and higher temperature.

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